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High Temperature Oxidation of E110G and E110 Fuel Claddings in Nitrogen-containing Atmospheres

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ABSTRACT

Experiments with E110G and E110 cladding specimens were carried out in different kinds of nitrogen-containing environment at high temperatures. The aim of these experiments is to obtain more detailed information on the zirconium fuel cladding behaviour under severe accident conditions and to provide adequate data for model developments. These tests are part of the Zirconium Material Science Studies (CAK) project. The sponge based- and the traditional types of fuel cladding rings were oxidised and/or nitrided in steam-nitrogen mixtures containing 4, 10, 50 and 100 vol% nitrogen. The tests were conducted under isothermal conditions at 1000 °C and 1200 °C. The impact of nitrogen on the high temperature oxidation kinetics and the microstructure of the claddings was investigated. Due to the formation of non-protective oxide layer the oxidation kinetics of E110 was faster in all steam-nitrogen mixtures than in pure steam. The experimental results showed different oxidation behaviour of E110G and E110 alloys in many cases. However, the mass increase of both claddings was very low in pure nitrogen atmosphere.

1 INTRODUCTION

Zirconium-based E110 alloy (Zr1%Nb) has been used as fuel cladding material in nuclear reactors. It has high mechanical strength and very good corrosion resistance during normal operation. However, oxidising atmosphere (steam, air) can evolve under accident conditions, which can lead to the rapid oxidation of the cladding. The presence of nitrogen in oxidising environment may intensify the oxidation process [1-6]. The oxidation strongly reduced the ductility and the load bearing capability of the cladding.

In order to study the effect of nitrogen on the high temperature oxidation kinetics and the microstructure of the claddings a new test series has been initiated at Hungarian Academy of Sciences, Centre for Energy Research (MTA EK). The purpose of this experiment is to get more detailed information on the zirconium fuel cladding behaviour under severe accident conditions and to provide adequate data for development of computer programs. These tests are part of the Zirconium Material Science Studies (CAK) project.

2 EXPERIMENTAL

2.1 Sample preparation

Traditional E110 alloy (produced by electrolytic method) and sponge base E110G alloy were investigated in all tests. The E110G alloy contains half the amount of impurities (70 ppm C, Si, Ni, P, Cl, N, F, Al) and more iron (500 ppm), compared to E110 [7]. The original fuel cladding tubes with 9.1 mm outer diameter were cut into 8 mm long specimens. The specimens were cleaned in acetone.

2.2 Equipment for oxidation tests

All experiments were conducted in a high temperature resistance tube furnace with steam generator and condenser. Figure 1 shows the schematic figure of test facility. These tests were performed in mixed steam-nitrogen atmospheres (96 vol% steam – 4 vol% nitrogen; 90 vol% steam – 10 vol% nitrogen; 50 vol% steam – 50 vol% nitrogen); in steam (using argon carrier gas) and in pure nitrogen at 1000 °C and 1200 °C. The steam flow rate was 2 – 5 mg/cm^2/s. It was determined by measuring the mass of the condensed water. In case of pure nitrogen atmosphere, the outlet nitrogen flow rate (5 mg/cm^2/s) was measured by a calibrated bubble gas flow meter. The samples were oxidized for different times (280 s – 3600 s) in a quartz boat. The extent of the oxidation was calculated on the basis of the mass increase.

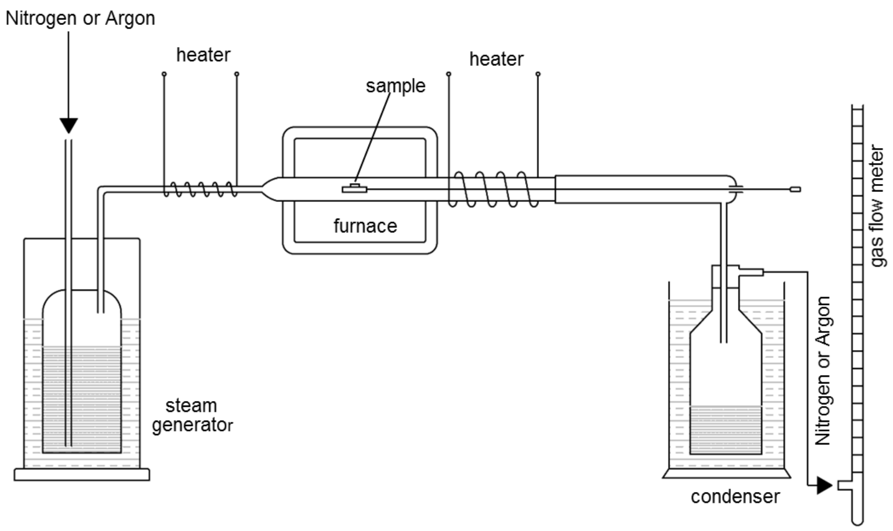

Figure 1: Scheme of the experimental set-up

2.3 Post-test examinations

Post-test examinations of the selected samples were conducted by scanning electron microscopy (SEM) and light optical microscopy. The selected samples were investigated both in as received state and by preparing their cross sections by embedding them into epoxy resin, then by grinding and polishing their surfaces. The SEM studies were performed at 5 kV accelerating voltage.

3 RESULTS

3.1 Oxidation tests

The mass gains during oxidation of E110 and E110G alloys in various nitrogen-containing steam atmospheres and in pure steam, at 1000 °C and 1200 °C are presented in Figure 2 and Figure 3. The oxidation of E110 cladding in all steam-nitrogen mixtures resulted in greater mass gain compared to pure steam, especially at 1000 °C. At this temperature, the presence of even small amount of nitrogen (4%) in the steam atmosphere led to accelerated oxidation (Figure 2) of E110. In case of E110G alloy, only the mixture containing high nitrogen content (50%) had significant effect on the oxidation (Figures 2 and 3). The mass increase of both alloys was very low in pure nitrogen environment.

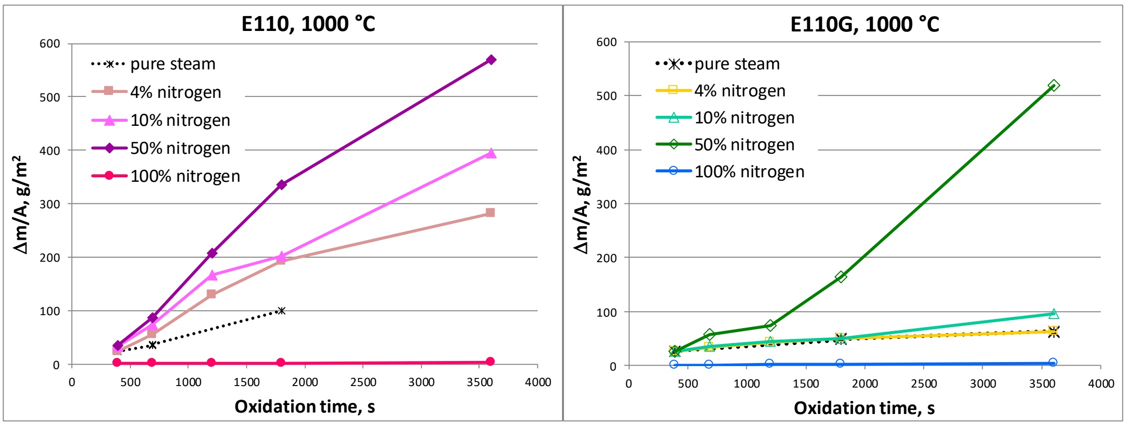

Figure 2: Oxidation kinetics of E110 and E110G in mixed steam-nitrogen atmosphere at 1000 °C

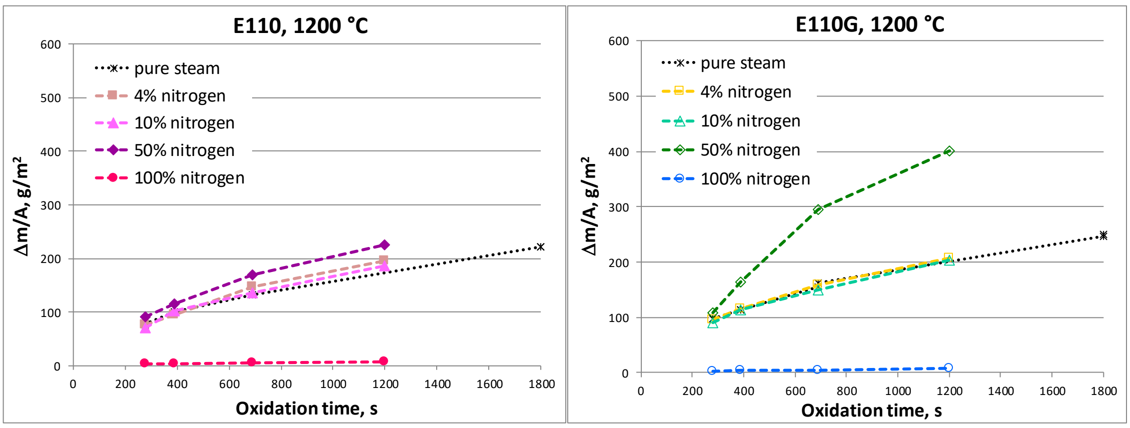

Figure 3: Oxidation kinetics of E110 and E110G in mixed steam-nitrogen atmosphere at 1200 °C

3.2 Post-test examinations

Figure 4 shows the post-test appearance and secondary electron images (SEI) of zirconium cladding samples oxidised in 50 % steam – 50 % nitrogen atmosphere.

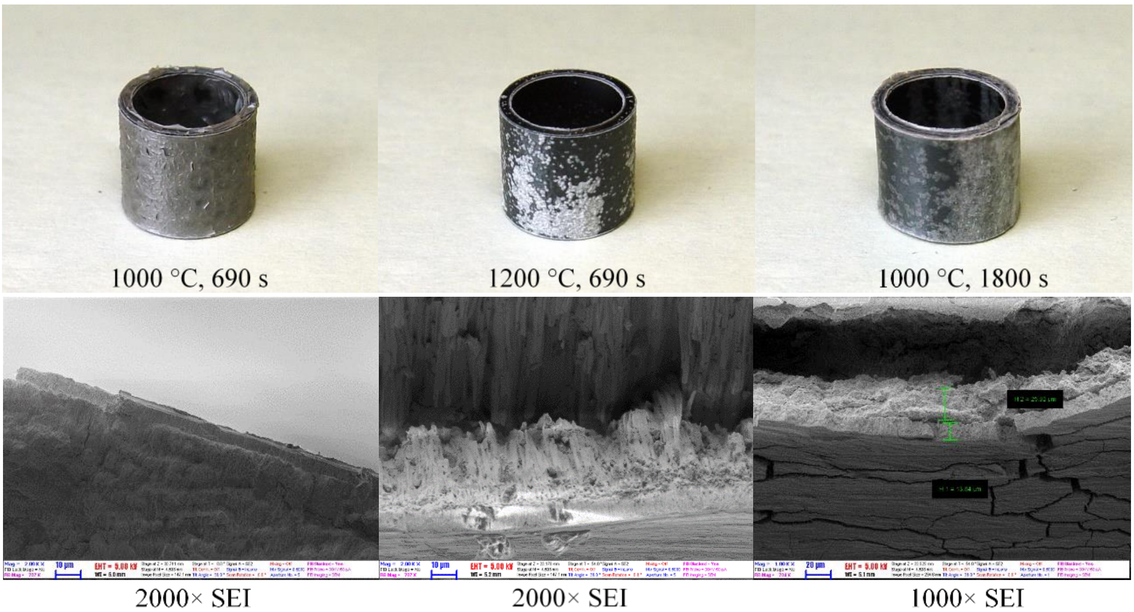

Figure 4: Post-test appearance and SEM images for the E110 (left and middle) and E110G (right) ring samples oxidised in steam-nitrogen mixture containing 50% nitrogen

Layered structure and the presence of relatively small sized cracks oriented almost in radial direction is typical for E110 sample oxidised for 690 s at 1000 °C (Figure 4, left), while large and smaller sized needle crystals are characteristic for E110 sample oxidised at 1200 °C (Figure 4, middle). Layered structure, huge cracks oriented almost parallel to the circumference of the ring sample, further some radial cracks are typical for E110G sample oxidised for 1800 s at 1000 °C (Figure 4, right).

In our earlier steam oxidation tests [8], compact and protective oxide layers were found on the cladding surface at 1200 °C. Our current results confirmed the deteriorating effect of nitrogen in the steam atmosphere on the oxide structure.

Figure 5 shows the optical micrographs of E110G samples oxidised for the same time (1200 s) at 1000 °C and 1200 °C, in 50 % steam – 50 % nitrogen mixture. In case of the sample oxidised at higher temperature (Figure 5, right) a much thicker outside oxide layer was formed and high amount of yellow-coloured nitride precipitates can be observed in this layer. Due to the high degree of oxidation at 1200 °C the β-phase zirconium was consumed and could not be observed.

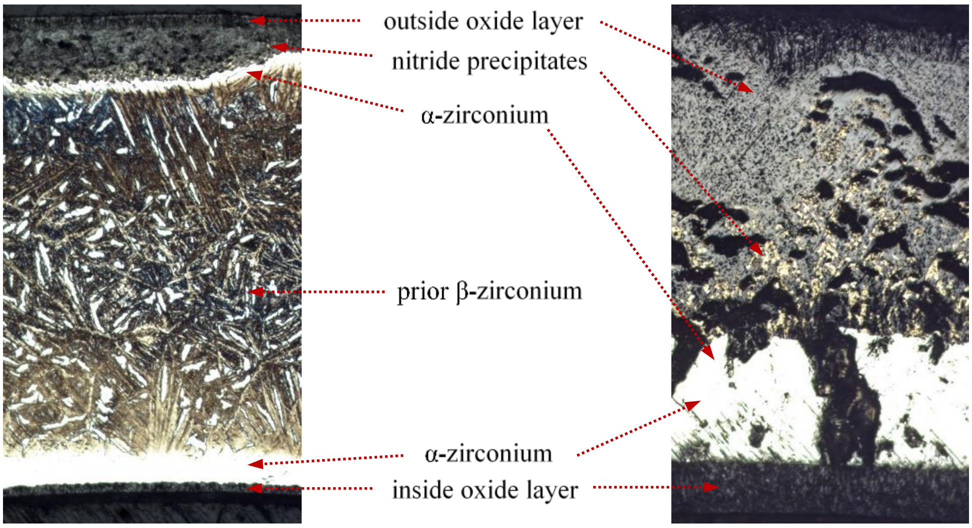

Figure 5: Total cross sections of E110G claddings oxidised for 1200 s at 1000 °C (left) and 1200 °C (right) in steam-nitrogen mixture containing 50% nitrogen

The micrographs of E110 samples oxidised for 1200 s at 1000 °C, in various mixtures of steam and nitrogen are shown in Figure 6. By studying the cross sections of these samples, differences in the presence of nitrides and also in the oxide morphology can be revealed. Yellow-coloured nitride is not visible on the first and second micrographs. The third one shows nitride precipitates close to the metal-oxide boundary when the nitrogen content was 50% in the steam.

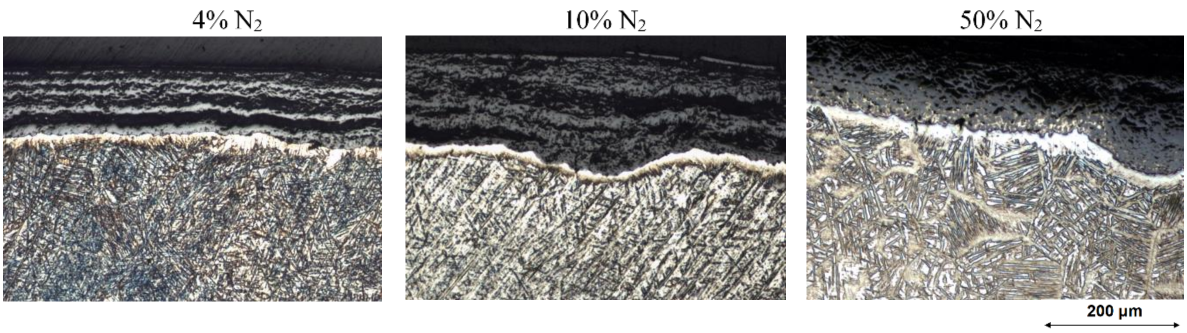

Figure 6: Cross sections of E110 claddings oxidised (1000 °C, 1200 s) in steam-nitrogen mixture containing 4%, 10% and 50% nitrogen

4 CONCLUSIONS

High temperature oxidation tests of zirconium-based fuel claddings were performed in nitrogen-containing atmospheres at 1000 and 1200 °C under isothermal conditions. The nitrogen contents of the steam were varied between 0 and 100 vol% nitrogen. The influence of nitrogen content on the oxidation kinetics and the oxide structure of the E110 and E110G alloys was confirmed. In case of E110 alloy at 1000 °C, even small amount of nitrogen in the steam atmosphere lead to significant acceleration of oxidation kinetics. Low nitrogen concentrations up to 10% had no similar effect for E110G alloy, since the more intense oxidation started only at 50% nitrogen content for this cladding type.

Nitride precipitations and different oxide morphology can be observed in the oxide of both alloys. The mass increase of these claddings was very low in pure nitrogen. These results provide important data for model developments to support NPP accident analyses and specification of boundary conditions for integral experiment.

ACKNOWLEDGMENTS

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REFERENCES

[1] Z. Hózer, P. Windberg, I. Nagy, L. Maróti, L. Matus, M. Horváth, A. P. Csordás, M. Balaskó, A. Czitrovszky, P. Jani, "Interaction of failed fuel rods under air ingress conditions, " Nuclear Technology, 141, 244-256 (2003).

[2] C. Duriez, M. Steinbrück, D. Ohai, T. Meleg, J. Birchley, T. Haste, "Separate-effect tests on zirconium cladding degradation in air ingress situations, " Nuclear Engineering and Design, 239, 244-253 (2009).

[3] Martin Steinbrück, "Prototypical experiments relating to air oxidation of Zircaloy-4 at high temperatures, " Journal of Nuclear Materials, 392, 531-544 (2009)

[4] O. Coindreau, C. Duriez, S. Ederli, "Air oxidation of Zircaloy-4 in the 600–1000 °C temperature range: Modeling for ASTEC code application, " Journal of Nuclear Materials, 405, 207-215 (2010)

[5] E. Perez-Feró, T. Novotny, M. Horváth, M. Kunstár, N. Vér, Z. Hózer, "High Temperature Behaviour of E110G and E110 Fuel Claddings in Various Mixtures of Steam and Air", WRFPM 2014 Water Reactor Fuel Performance Meeting /Top Fuel/ LWR Fuel Performance Meeting, 14-17 September 2014, Sendai, Japan

[6] Martin Steinbrueck, "Fabio Oliveira da Silva, Mirco Grosse Oxidation of Zircaloy-4 in steam-nitrogen mixtures at 600–1200 °C", Journal of Nuclear Materials, 490, 226-237 (2017)

[7] S. A. Nikulin, A.B. Rozhnov, V.A. Belov, E.V. Li, V.S. Glazkina, "Influence of chemical composition of zirconium alloy E110 on embrittlement under LOCA condition – Part 1: Oxidation kinetics and macrocharacteristics of structure and fracture, " Journal of Nuclear Materials, 418, 1-7 (2011)

[8] Erzsébet Perez-Feró, Tamás Novotny, Anna Pintér-Csordás, Mihály Kunstár, Zoltán Hózer, Márta Horváth, Lajos Matus, "Experimental results on the breakaway oxidation of the E110 cladding alloy under high-temperature isothermal conditions", Progress in Nuclear Energy, 2016. Volume 93, pp 89-95